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Influence of Microwave Irradiation on Calcium Sulphate Crystal Phase

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In present studies, a special experiment system was designed to obtain calcium sulphate crystal under the similar temperature-profile increase in microwave heating and traditional heating by water bath. The main products heated by water bath heating are calcium sulphate dihydrates, but a small quantity of calcium sulphate hemihydrates are detected with microwave heating. By multiphysics calculation and experimental measurement, the results show that this difference is not induced by non-thermal effect and calcium sulphate hemihydrates induced by hot spot during the microwave heating.

Key Words: Calcium sulphate crystal, Microwave heating, Phase, Hot spot.

INTRODUCTION

Industrial use of microwave radiation as an alternative to conventional thermal heating has generated interest recently mainly because of the drastic reduction in the processing time[1-3]. Even though microwaves have found a wide application, its chemical mechanism of interaction with the irradiated material has not been well understood. Some recent studies have demonstrated that microwaves are capable of bringing the non-thermal effects[4-8]. Loupy[9] believed the microwave non-thermal effects do indeed exist, even if it cannot yet be adequately explained. Oppositely, some studies have concluded that there is no evidence to support the existence of microwave non-thermal effects[10]. In this paper, we design a system to obtain calcium sulphate crystal under the 'similar temperature-profile' increase in microwave heating and traditional heating by water bath. The main products heated by water bath are calcium sulphate dihydrates, but a small quantity of calcium sulphate hemihydrates are detected with microwave heating. It is well known that calcium sulphate hemihydrates can only be produced above 107 ºC. By multiphysics calculation and experimental measurement, the results show that calcium sulphate hemihydrates induced by hot spot during the microwave heating. This difference is not induced by non-thermal effect. There are quite difference between the measured macroscopical temperature of the reaction system and local temperature during the high power microwave heating.

EXPERIMENTAL

Calcium sulphate crystals are produced by the reaction as follows:

$$H_2SO_4 + CaCl_2 \longrightarrow CaSO_4 + 2HCl \quad (1)$$

The initial concentrations were $C_{H_2SO_4} = 0.2$ M/L and $C_{CaCl_2} = 0.2$ M/L. Improved Glanz microwave oven (700 W, 2.45 GHz) and KXS-A trough were separately used to heat the reaction. In order to accurately measure the temperature, we make use of UMI-8 optical thermometer to get the temperature rise. The experimental system is shown in Fig. 1.

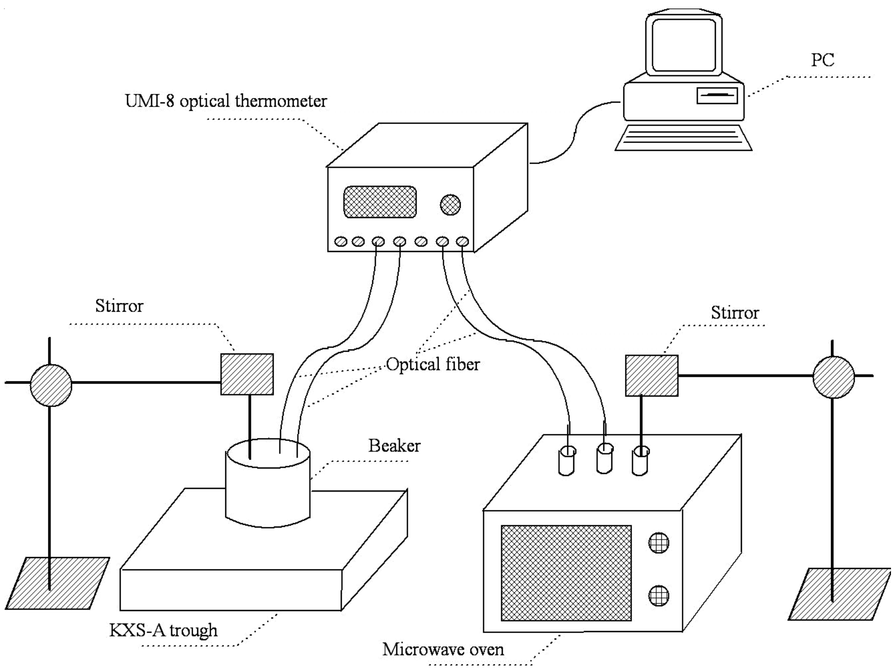


Fig. 1. Experimental system

In order to achieve the "similar temperature-profile" increase throughout the reaction with microwave heating to the one with traditional heating by water bath, the power of microwave oven can be controlled by using a circuit with the feed back of temperature from the optical fiber thermometer. The solutions are stirred in both heating methods. The curves of temperature rise with two heating methods are shown in Fig. 2.

After the reaction, the calcium sulphate crystals were dried below 60 ºC for 12 h and analyzed by XRD. The XRD pattern of calcium sulphate crystal is shown in Fig. 3. The main products heated by water bath are calcium sulphate dihydrates, but a small quantity of calcium sulphate hemihydrates are detected with microwave heating. It is well known that calcium sulphate hemihydrates can only be produced above 107 ºC. So, it is suggested that the hot spots may be come during the microwave heating on reaction solution.

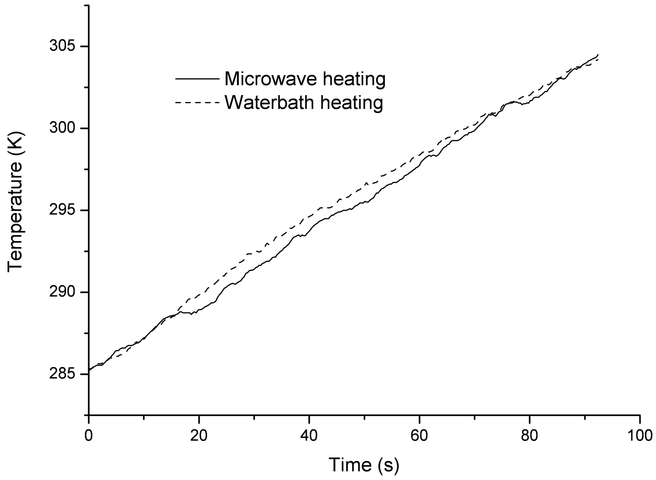


Fig. 2. Curves of temperature rise with two heating method

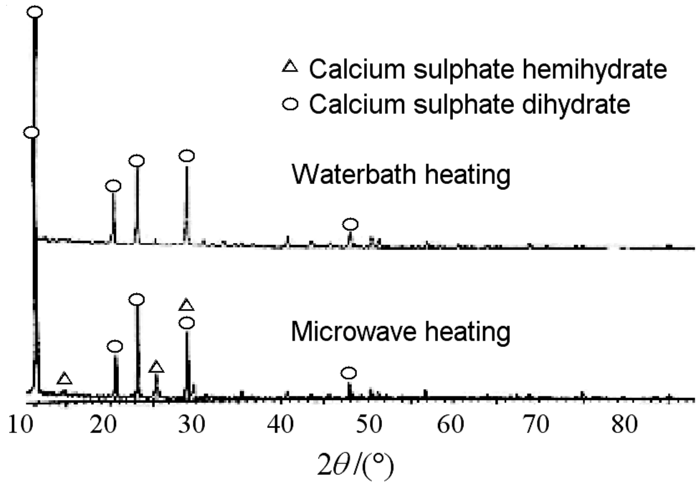


Fig. 3. XRD pattern of calcium sulphate crystals

The phenomenon of rupture in the solution's surface is also observed. So, the ruptured calcium sulphate crystal was analyzed by XRD, too. The XRD pattern of ruptured calcium sulphate crystal is shown in Fig. 4. There are many calcium sulphate hemihydrates, from Fig. 4, only a few of calcium sulphate dimihydrates are detected.

Multiphysics calculation: There exists some specific effect during the microwave heating probably because of the existence of hot spots. A numerical model was presented to study the microwave heating on calcium sulphate crystallization. The coupled Maxwell's equations, fluid field equations and heat transport equations were solved by using finite-element (FEM) method. The flow chart of the numerical simulation of multiphysics is shown in Fig. 5.

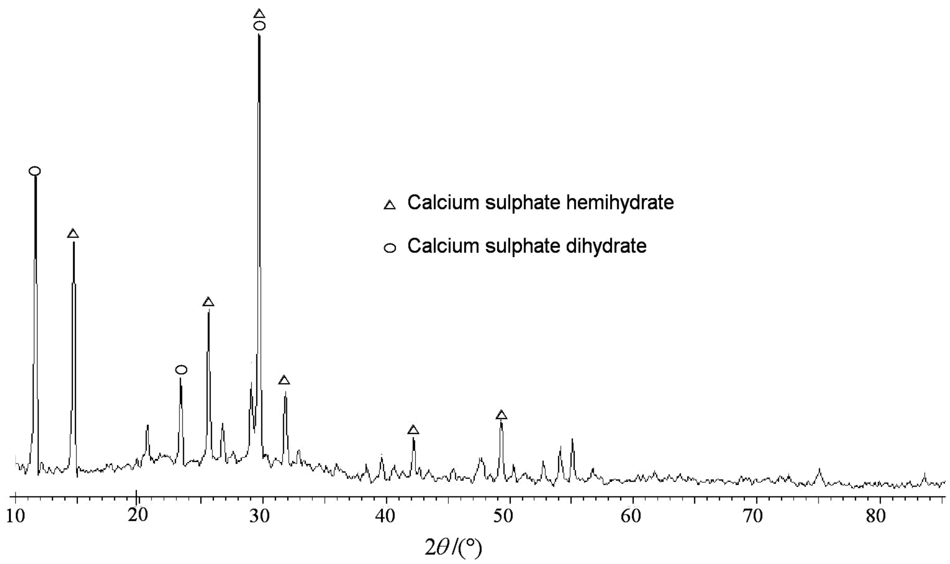


Fig. 4. XRD pattern of ruptured calcium sulphate crystals

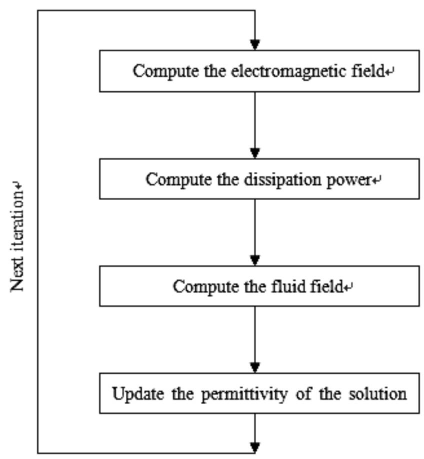


Fig. 5. Flow chart of the numerical simulation of multiphysics

The numerical simulation model is shown in Fig. 6. The modified Galanz household microwave oven is used as a microwave chemical reactor. The glass stirrer located in the center of the beaker and the space from its bottom was 10 mm. The speed of stirrer was 50 r/min and its size was 50 mm × 10 mm × 20 mm, the radius of rotation axis was 3.25 mm and the length was 30mm. The others sizes are shown in Fig. 6 (note: the origin of coordinate was located at the center on the bottom interface of the beaker).

The calculated results of the temperature distribution on the top interface of reaction solution heated by microwave at different time are shown in Fig. 7.

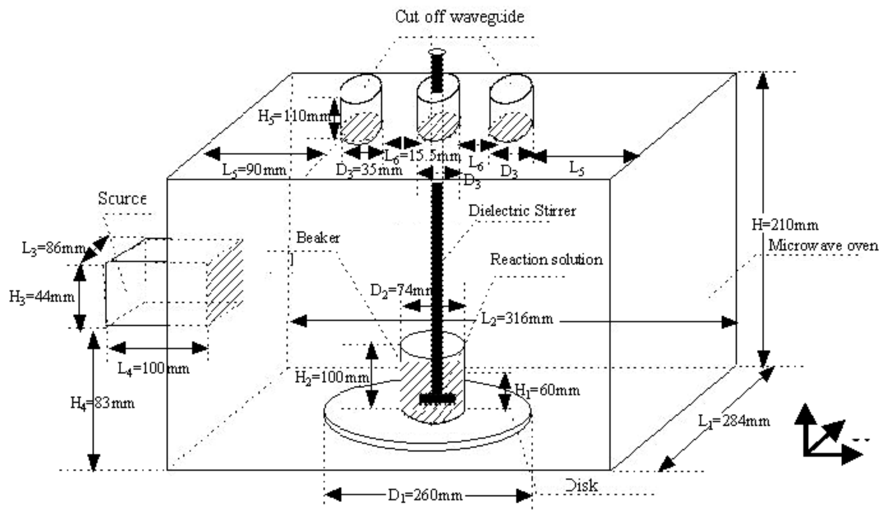
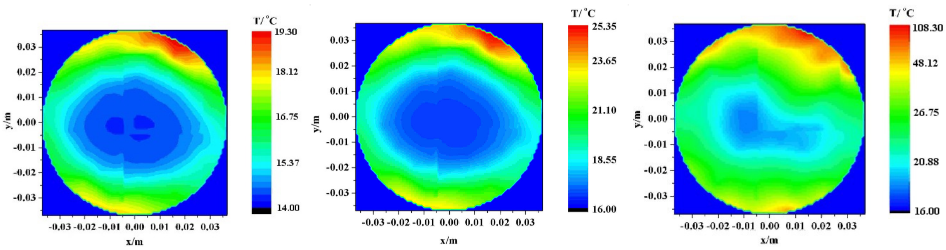


Fig. 6. Numerical simulation model



(a) (b) (c)

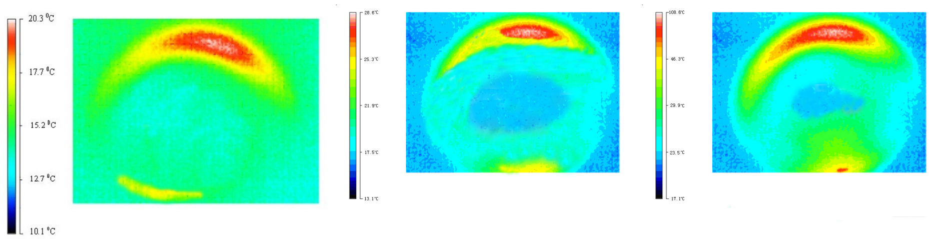
Fig. 7. Calculated temperature distribution on the top interface of reaction solution heated by microwave at different time: (a) 5 s, (b) 15 s, (c) 45 s

Some hot spots exist in the top interface (Fig. 7) and its temperature up to above 107 ºC during the microwave heating on reaction solution. It is well known that calcium sulphate hemihydrates can only be produced above 107 ºC. So, the calculated results show that calcium sulphate hemihydrates can be induced by hot spots during the microwave heating.

Experiment results: To verity the calculated results, we repeated the above-mentioned experiment and use Thermo View Ti30 to obtain the distribution of temperature on the top interface of solution. The approximately agreement can be seen between the measured and calculated results (Fig. 8). Certainly, there exist some hot spots above the 107 ºC during the microwave heating on reaction solution.

Conclusion

Under the 'similar temperature-profile', the main products heated by water bath heating are calcium sulphate dihydrates, but a small quantity of calcium sulphate hemihydrates are detected with microwave heating. By multiphysics calculation and experimental measurement, the results show that calcium sulphate hemihydrates



(a) (b) (c)

Fig. 8. Measured temperature distribution on the top interface of reaction solution heated by microwave at different time: (a) 5 s, (b) 15 s, (c) 45 s

induced by hot spot during the microwave heating. This difference is not induced by non-thermal effect. There are quite difference between the measured macro-scopical temperature of the reaction system and local temperature at high power microwave heating.

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